Critical phenomena and critical relations

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Abstract

We consider systems which exhibit typical critical dependence of the specific heat: $\Delta c \propto (T_C - T)^{-\gamma}$ ($T < T_C$); $\Delta c \propto (T - T_C)^{-\gamma'}$ ($T > T_C$) where γ, γ' are critical exponents ($\gamma = \alpha$ for $\Delta c = \Delta c_{p,N}$, $\gamma = \overline{\alpha}$ for $\Delta c = \Delta c_{V,N}$), as well as, the case when $\Delta c \propto (\ln \mid T_C - T \mid)^a$ ($a = \frac{1}{3}$, uniaxial ferroelectrics; $a = 1$, liquid He^4). Starting from the critical behaviour of the specific heat we find the Gibbs (Helmholtz) potential in the vicinity of the critical point for each case separately. We derive in this way many exact critical relations in the limit $T \to T_C$ which remain the same for each considered case. They define a new class of universal critical relations independent from the underlying microscopic mechanism and the symmetry of these systems. The derived relations are valid for a very broad class of magnetic, ferroelectric and superconducting materials, as well as, for liquid He^4.

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1 Introduction

Critical phenomena in solids, connected with second order phase transitions, belong to very attractive and intriguing problems in physics. Many theoretical models and methods have been applied to resolve these interesting questions (cf e.g. Refs [1]-[5] for a review and the original papers cited therein), however, the most important, general and successfull method, applied in this area of physics, seems to be still the phenomenological approach, initiated by the pioneer works of Landau, Refs [6], [7]. This approach has succsessfully been applied to superconducting systems resulting in many useful critical relations, derived in Ref. [8]. For many other systems (magnetic, ferroelectric, liquid He^4, etc.) this approach unfortunately fails because of critical exponents (cf e.g. Refs [1]-[5]). We can, however, improve this approach and calculate the

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Gibbs (Helmholtz) potential near the critical point from the observed specific heat anomaly ($T < T_C$; $T > T_C$). Similarly to Ref. [8] we include into the considerations the critical behaviour of the chemical potential as indicator of phase transitions in a more general sense (see Ref. [8] and papers cited therein). We derive in this way many interesting thermodynamical relations (cross-relations) at the critical point in the limit $T \to T_C$. These exact relations seem to be of fundamental importance for critical phenomena in solids and should generally be valid for a very broad class of magnetic or ferroelectric systems, as well as, for superconducting systems as a special case. Surprisingly, they are also valid in the case of logarithmic divergence of the specific heat (uniaxial ferroelectrics and liquid He^4). The derived relations possess very similar form to the critical relations presented in Ref. [8] and define a new class of exact relations at the critical point independent from the underlying microscopic mechanism leading to second order phase transitions and independent from the symmetry of the system.

2 Phenomenological Gibbs (Helmholtz) potentials and critical relations

Performing experimental measurements of the temperature dependence of the specific heat $c_{p,N}$ at constant pressure p and constant number of particles N we can find that for magnetic, ferroelectric or superconducting systems $c_{p,N}$ exhibits a pronounced anomaly at the critical point $T = T_C$ (cf e.g. Refs [1]-[5]). Independently from the considered system (here: magnetic, ferroelectric or superconducting) it is convenient to introduce a reference system which possesses exactly the same structure (symmetry), atomic masses, etc., the specific heat of this system $c_{p,N}^{(0)}$ exhibits, however, no anomaly at $T = T_C$. Let us introduce an auxiliary quantity

$$\Delta c_{p,N}(T) \equiv c_{p,N}(T) - c_{p,N}^{(0)}(T). \tag{1}$$

A very broad class of materials (magnetic, ferroelectric or superconducting) shows a general, critical behaviour (see e.g. [1]-[5]) of the type[1]

$$\Delta c_{p,N}(T) \propto \begin{cases} (T_C - T)^{-\alpha}, & T < T_C \\ (T - T_C)^{-\alpha'}, & T > T_C \end{cases} \tag{2}$$

where α, α' are critical exponents, depending on the material (α, $\alpha' > 0$). For magnetic and ferroelectric systems $\Delta c_{p,N}$ usually diverges at the critical point, for superconducting ones $\Delta c_{p,N}$ exhibits only a finite jump. For simplicity, we

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[1]The case of the logarithmic divergence of the specific heat will be considered in the next Section.

restrict ourselves to the case $T < T_C$ and we assume (see expression (2)) that in the vicinity of the critical point

$$\Delta c_{p,N}(T) = A(p, N)(T_C - T)^{-\alpha} \tag{3}$$

where $A(p, N)$ is a parameter. The critical temperature T_C should also be considered as a function of p and N ($T_C = T_C(p, N)$), as suggested by experimental results. The thermodynamics of the system in the vicinity of the critical point ($T < T_C$) can be described by the Gibbs potential $Z(T, p, N)$. We can formally write

$$Z(T, p, N) = Z_0(T, p, N) + \Delta Z \tag{4}$$

where

$$\Delta Z = Z - Z_0, \tag{5}$$

Z_0 is the Gibbs potential of the reference system and $c_{p,N}^{(0)} = -T \left(\frac{\partial^2 Z_0}{\partial T^2} \right)_{p,N}$. The analytical form of ΔZ should necessarily be chosen in such a way that the thermodynamical relation

$$\Delta c_{p,N} = -T \left(\frac{\partial^2 (\Delta Z)}{\partial T^2} \right)_{p,N} \tag{6}$$

reproduces the critical behaviour of $\Delta c_{p,N}$, given by the formula (3). It is easy to find that the leading term of ΔZ should have the general form[2]

$$\Delta Z = D(p, N)(T_C - T)^{2-\alpha} \tag{7}$$

where $D(p, N)$ is a parameter. Really, when applying (6) and (7) we obtain

$$
\begin{aligned}
\Delta c_{p,N} &= -T(2 - \alpha)(1 - \alpha)D(p, N)(T_C - T)^{-\alpha} \\
&\approx -T_C(2 - \alpha)(1 - \alpha)D(p, N)(T_C - T)^{-\alpha} \\
&= A(p, N)(T_C - T)^{-\alpha}
\end{aligned}
\tag{8}
$$

where

$$A(p, N) = -T_C(2 - \alpha)(1 - \alpha)D(p, N). \tag{9}$$

Thus, the asymptotic form of the Gibbs potential (4) in the vicinity of the critical point ($T < T_C$) has to be equal to

$$Z(T, p, N) = Z_0(T, p, N) + D(p, N)(T_C - T)^{2-\alpha}. \tag{10}$$

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[2]It is possibly to find ΔZ exactly when integrate the expression (6) with the use of the formula (3). The result is given in the Appendix A. To avoid the presentation of very long expressions we restrict ourselves to consider only the leading term in ΔZ, given by the formula (7). This approach (see Appendix A) leads to the same, exact critical relations (18)-(22) as in the case when the complete expression for ΔZ (see the formula (A.6)) is used.

The phenomenological relations (3) and (10), resulting from the experimental, critical behaviour of a broad class of systems can easily be used to derive many critical relations. The chemical potential $\mu = (\frac{\partial Z}{\partial N})_{T,p}$ ($\mu_0 = (\frac{\partial Z_0}{\partial N})_{T,p}$) and the volume of the system $V = (\frac{\partial Z}{\partial p})_{T,N}$ ($V_0 = (\frac{\partial Z_0}{\partial p})_{T,N}$) can easily be found from (10). We obtain

$$
\begin{aligned}
\mu &= \mu_0 + \left(\frac{\partial D}{\partial N}\right)_p (T_C - T)^{2-\alpha} \\
&+ (2-\alpha)D(T_C - T)^{1-\alpha}\left(\frac{\partial T_C}{\partial N}\right)_p
\end{aligned}
\tag{11}
$$

and

$$
\begin{aligned}
V &= V_0 + \left(\frac{\partial D}{\partial p}\right)_N (T_C - T)^{2-\alpha} \\
&+ (2-\alpha)D(T_C - T)^{1-\alpha}\left(\frac{\partial T_C}{\partial p}\right)_N
\end{aligned}
\tag{12}
$$

where we have taken into account that $T_C = T_C(p, N)$. With the use of (11) and (12) we obtain

$$
\begin{aligned}
\Delta\left(\frac{\partial \mu}{\partial T}\right)_{p,N} &= -(T_C - T)^{-\alpha}(2-\alpha)\,[\,\left(\frac{\partial D}{\partial N}\right)_p (T_C - T) \\
&+ (1-\alpha)D \cdot \left(\frac{\partial T_C}{\partial N}\right)_p \,],
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
\Delta\left(\frac{\partial V}{\partial T}\right)_{p,N} &= -(T_C - T)^{-\alpha}(2-\alpha)\,[\,\left(\frac{\partial D}{\partial p}\right)_N (T_C - T) \\
&+ (1-\alpha)D \cdot \left(\frac{\partial T_C}{\partial p}\right)_N \,],
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
\Delta\left(\frac{\partial \mu}{\partial p}\right)_{T,N} &= (T_C - T)^{-\alpha}\Big\{\frac{\partial^2 D}{\partial p \partial N}(T_C - T)^2 \\
&+ (2-\alpha)(T_C - T)\Big[\left(\frac{\partial D}{\partial N}\right)_p\left(\frac{\partial T_C}{\partial p}\right)_N \\
&+ \left(\frac{\partial D}{\partial p}\right)_N\left(\frac{\partial T_C}{\partial N}\right)_p + D \cdot \left(\frac{\partial^2 T_C}{\partial p \partial N}\right)\Big] \\
&+ (2-\alpha)(1-\alpha)D \cdot \left(\frac{\partial T_C}{\partial p}\right)_N\left(\frac{\partial T_C}{\partial N}\right)_p\Big\},
\end{aligned}
\tag{15}
$$

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$$\Delta\left(\frac{\partial\mu}{\partial N}\right)_{T,p} = (T_C - T)^{-\alpha}\Big\{\left(\frac{\partial^2 D}{\partial N^2}\right)_p (T_C - T)^2$$
$$+(2-\alpha)(T_C - T)\Big[2\left(\frac{\partial D}{\partial N}\right)_p\left(\frac{\partial T_C}{\partial N}\right)_p + D\cdot\left(\frac{\partial^2 T_C}{\partial N^2}\right)_p\Big]$$
$$+(2-\alpha)(1-\alpha)D\cdot\Big[\left(\frac{\partial T_C}{\partial N}\right)_p\Big]^2\Big\} \qquad (16)$$

and

$$\Delta\left(\frac{\partial V}{\partial p}\right)_{T,N} = (T_C - T)^{-\alpha}\Big\{\left(\frac{\partial^2 D}{\partial p^2}\right)_N (T_C - T)^2$$
$$+(2-\alpha)(T_C - T)\Big[2\left(\frac{\partial D}{\partial p}\right)_N\left(\frac{\partial T_C}{\partial p}\right)_N + D\cdot\left(\frac{\partial^2 T_C}{\partial p^2}\right)_N\Big]$$
$$+(2-\alpha)(1-\alpha)D\cdot\Big[\left(\frac{\partial T_C}{\partial p}\right)_N\Big]^2\Big\} \qquad (17)$$

where $\Delta X \equiv X(T) - X_0(T)$ has exactly the same interpretation as in the formula (1). It is interesting to note that for magnetic (ferroelectric) systems $\Delta c_{p,N}$, $\Delta(\frac{\partial\mu}{\partial T})_{p,N}$, $\Delta(\frac{\partial V}{\partial T})_{p,N}$, $\Delta(\frac{\partial\mu}{\partial p})_{T,N}$, $\Delta(\frac{\partial\mu}{\partial N})_{T,p}$ and $\Delta(\frac{\partial V}{\partial p})_{T,N}$, generally, diverge at the critical point. However, when e.g. divide (13)-(17) by (3) the "dangerous" term $(T_C - T)^{-\alpha}$ cancels out (see also (9)) and taking the limit $T \to T_C^-$ we obtain the following relations

$$\lim_{T\to T_C^-}\frac{\Delta(\frac{\partial\mu}{\partial T})_{p,N}}{\Delta c_{p,N}} = \left(\frac{\partial\ln T_C}{\partial N}\right)_p, \qquad (18)$$

$$\lim_{T\to T_C^-}\frac{\Delta(\frac{\partial V}{\partial T})_{p,N}}{\Delta c_{p,N}} = \left(\frac{\partial\ln T_C}{\partial p}\right)_N, \qquad (19)$$

$$\lim_{T\to T_C^-}\frac{\Delta(\frac{\partial\mu}{\partial p})_{T,N}}{\Delta c_{p,N}} = -\left(\frac{\partial\ln T_C}{\partial N}\right)_p\left(\frac{\partial T_C}{\partial p}\right)_N, \qquad (20)$$

$$\lim_{T\to T_C^-}\frac{\Delta(\frac{\partial\mu}{\partial N})_{T,p}}{\Delta c_{p,N}} = -\left(\frac{\partial\ln T_C}{\partial N}\right)_p\left(\frac{\partial T_C}{\partial N}\right)_p \qquad (21)$$

and

$$\lim_{T\to T_C^-}\frac{\Delta(\frac{\partial V}{\partial p})_{T,N}}{\Delta c_{p,N}} = -\left(\frac{\partial\ln T_C}{\partial p}\right)_N\left(\frac{\partial T_C}{\partial p}\right)_N. \qquad (22)$$

It, however, means that the limits exist and the derived relations are exact[3]. For classic superconductors ($\alpha = 0$) all the quantities (3) and (13)-(17) are finite

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[3]The additional terms to ΔZ (see Appendix A) modify only the expressions (11)-(17). By forming the quotients (18)-(22) in the limit $T \to T_C^-$ their contribution is equal to zero (see Appendix A) and therefore the critical relations (18)-(22) are, in fact, exact.

and therefore we can drop the $\lim\limits_{T \to T_C^-}$ in the expressions (18)-(22) and we obtain the formulae (29)-(33) from Ref. [8]. In orther words the formulae (18)-(22) are valid for a broad class of magnetic, ferroelectric and superconducting systems. Because of Maxwell relations $\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}$, $\left(\frac{\partial S}{\partial N}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N}$ and $\left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ there are only five independent relations of the type (13)-(17). Because $\Delta\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\Delta\left(\frac{\partial V}{\partial T}\right)_{p,N}$, $\Delta\left(\frac{\partial S}{\partial N}\right)_{T,p} = -\Delta\left(\frac{\partial \mu}{\partial T}\right)_{p,N}$ and $\Delta\left(\frac{\partial V}{\partial N}\right)_{T,p} = \Delta\left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ the corresponding critical relation with the presence of $\Delta\left(\frac{\partial S}{\partial p}\right)_{T,N}$, $\Delta\left(\frac{\partial S}{\partial N}\right)_{T,p}$ and $\Delta\left(\frac{\partial V}{\partial N}\right)_{T,p}$ can easily be obtained from (19),(18) and (20), respectively. Besides, it is very easy to obtain many other relations when e.g. divide (14) by (13) and take the limit

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial V}{\partial T})_{p,N}}{\Delta(\frac{\partial \mu}{\partial T})_{p,N}} = \frac{(\frac{\partial T_C}{\partial p})_N}{(\frac{\partial T_C}{\partial N})_p} \tag{23}$$

and so on. Therefore there is no need to write all of them explicitely here. It is also possible to calculate the derivatives $(\frac{\partial T_C}{\partial N})_p$, $(\frac{\partial T_C}{\partial p})_N$ from the relations (18), (19) and isert them into (20)-(22). In such a way we obtain cross-relations

$$\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial p}\right)_{T,N}}{\Delta c_{p,N}} = -T_C\Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial T}\right)_{p,N}}{\Delta c_{p,N}}\Big] \cdot \Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial V}{\partial T}\right)_{p,N}}{\Delta c_{p,N}}\Big] \tag{24}$$

$$\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial N}\right)_{T,p}}{\Delta c_{p,N}} = -T_C\Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial T}\right)_{p,N}}{\Delta c_{p,N}}\Big]^2 \tag{25}$$

and

$$\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial V}{\partial p}\right)_{T,N}}{\Delta c_{p,N}} = -T_C\Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial V}{\partial T}\right)_{p,N}}{\Delta c_{p,N}}\Big]^2. \tag{26}$$

In the case of superconducting systems we can drop the $\lim\limits_{T \to T_C^-}$ and the formulae (24)-(26) coincide with the formulae (34)-(36) from Ref. [8]. There are, however, again many other possibilities to form similar cross-relations which can be found with ease when starting from the formulae (3), (9) and (13)-(17).

We can also derive additional relations for systems at constant volume V. Similarly to (2) we can write (cf e.g. [1]-[5])

$$\Delta c_{V,N}(T) \propto \begin{cases} (T_C - T)^{-\overline{\alpha}}, & T < T_C \\ (T - T_C)^{-\overline{\alpha'}}, & T > T_C \end{cases} \tag{27}$$

where $\overline{\alpha}$ and $\overline{\alpha'}$ are critical exponents. We restrict ourselves again to the vicinity of the critical point for $T < T_C$ and we can assume that

$$\Delta c_{V,N} = \overline{A}(V,N)(T_C - T)^{-\overline{\alpha}} \tag{28}$$

where $\overline{A}(V,N)$ is a parameter. The corresponding leading term of the Helmholtz free energy has to be in the form (cf also (10))

$$F(T,V,N) = F_0(T,V,N) + \overline{D}(V,N)(T_C - T)^{2-\overline{\alpha}} \tag{29}$$

with $\overline{D}(V,N)$ as a parameter and $T_C = T_C(V,N)$. Here F_0 can be interpreted as the Helmholtz potential of the reference system. Repeating the calculations with the use of (29), quite similar to the presented above with the use of the Gibbs potential (cf (11)-(17)), we can find the exact relations similar to (18)-(22)[4]. We obtain

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial \mu}{\partial T})_{V,N}}{\Delta c_{V,N}} = \left(\frac{\partial \ln T_C}{\partial N}\right)_V, \tag{30}$$

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial p}{\partial T})_{V,N}}{\Delta c_{V,N}} = -\left(\frac{\partial \ln T_C}{\partial V}\right)_N, \tag{31}$$

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial \mu}{\partial V})_{T,N}}{\Delta c_{V,N}} = -\left(\frac{\partial \ln T_C}{\partial N}\right)_V \left(\frac{\partial T_C}{\partial V}\right)_N, \tag{32}$$

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial \mu}{\partial N})_{T,V}}{\Delta c_{V,N}} = -\left(\frac{\partial \ln T_C}{\partial N}\right)_V \left(\frac{\partial T_C}{\partial N}\right)_V, \tag{33}$$

and

$$\lim_{T \to T_C^-} \frac{\Delta(\frac{\partial p}{\partial V})_{T,N}}{\Delta c_{V,N}} = \left(\frac{\partial \ln T_C}{\partial V}\right)_N \left(\frac{\partial T_C}{\partial V}\right)_N. \tag{34}$$

There are again only five exact expressions of this type because of the Maxwell relations $\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial p}{\partial T}\right)_{V,N}$, $\left(\frac{\partial S}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N}$ and $\left(\frac{\partial p}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}$. There exists also a freedom to form another quotiens what results in many other expressions easy to obtain (we don't write them explicitly here). The analogous cross-relations, similar to (24)-(26) have the form

$$\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial V}\right)_{T,N}}{\Delta c_{V,N}} = T_C \Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial \mu}{\partial T}\right)_{V,N}}{\Delta c_{V,N}} \Big] \cdot \Big[\lim_{T \to T_C^-} \frac{\Delta\left(\frac{\partial p}{\partial T}\right)_{V,N}}{\Delta c_{V,N}} \Big], \tag{35}$$

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[4]The same critical relations (30)-(34) can also be obtained with the use of the exact Helmholtz potential, similarly to systems at constant pressure p (see Appendix A) and therefore the formulae (30)-(34) are exact.

$$\lim_{T \to T_C^-} \frac{\Delta \left(\frac{\partial \mu}{\partial N} \right)_{T,V}}{\Delta c_{V,N}} = -T_C \Big[\lim_{T \to T_C^-} \frac{\Delta \left(\frac{\partial \mu}{\partial T} \right)_{V,N}}{\Delta c_{V,N}} \Big]^2 \qquad (36)$$

and

$$\lim_{T \to T_C^-} \frac{\Delta \left(\frac{\partial p}{\partial V} \right)_{T,N}}{\Delta c_{V,N}} = T_C \Big[\lim_{T \to T_C^-} \frac{\Delta \left(\frac{\partial p}{\partial T} \right)_{V,N}}{\Delta c_{V,N}} \Big]^2. \qquad (37)$$

The other cross-relations are also very easy to find. In the case of supercon-ducting systems we can drop the $\lim_{T \to T_C^-}$ in these expressions and we obtain the formulae (46)-(53) from Ref. [8]. Similar calculations can also be repeated in the vicinity of the critical point for the case $T > T_C$, using the form of the spe-cific heat for this case (see (2) and (27)). It leads, however, to the same critical expressions (18)-(22), (24)-(26) and (30)-(37) where the limit $T \to T_C^-$ should be replaced by $T \to T_C^+$. In other words, we can replace in all these expressions the limit $T \to T_C^-$ by a more general form $\lim_{T \to T_C}$.

3 Logarithmic anomaly of the specific heat

It is interesting to see whether the derived critical relations (18)-(22), (24)-(26) and (30)-(37) are also valid in the case of logarithmic divergence of the specific heat, when

$$\Delta c_{p,N}(T) \propto (\ln(T_C - T))^a \qquad (38)$$

where $a = \frac{1}{3}$ for uniaxial ferroelectrics (see e.g. Ref. [5], p. 384) or $a = 1$ for liquid He^4 (see e.g. Refs [1], [9])[5].
For simplicity, we restrict ourselves to the case $T < T_C$ where

$$\Delta c_{p,N}(T) = A(p,N)[\ln(T_C - T)]^a \qquad (39)$$

and $A(p,N)$ is a parameter. It is easy to see that the leading term of the Gibbs potential, deduced from the expressions (6) and (39) should have the form[6]

$$Z(T,p,N) = Z_0(T,p,N) - \frac{1}{2}D(p,N)(T_C - T)^2[\ln(T_C - T)]^a \qquad (40)$$

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[5]According to different authors for liquid He^4 the formula (2) can also be valid for α, α' very small (cf e.g. [3] and papers cited therein). Thus, the critial relations, derived in the preceding Section are authomatically valid in this case.

[6]The exact form for ΔZ is given in Appendix B. Similarly to the preceding Section, the additional terms in ΔZ does not contribute to the final relations (18)-(22) which remain exactly the same. Because of extremally long expressions we present here only the calculations resulting from the leading term in the formula (40).

where $D(p, N)$ is a parameter. Applying the formulae (5) and (6) we obtain

$$\Delta c_{p,N}(T) = TD(p,N)\{[\ln(T_C - T)]^a$$
$$+ \frac{3a}{2}[\ln(T_C - T)]^{a-1} + \frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\}. \quad (41)$$

In the vicinity of the critical point the second and third term in the parenthesis of (41) can completely be neglected ($a = \frac{1}{3}, 1$) in comparison to the first, singular term. Thus, we can write

$$\Delta c_{p,N}(T) \approx TD(p,N)[\ln(T_C - T)]^a \approx T_C D(p,N)[\ln(T_C - T)]^a. \quad (42)$$

In other words the formula for the Gibbs potential (40) reproduces the critical behaviour of the specific heat (39) when we assume that

$$A(p, N) = T_C D(p, N). \quad (43)$$

The chemical potential $\mu = (\frac{\partial Z}{\partial N})_{T,p}$ ($\mu_0 = (\frac{\partial Z_0}{\partial N})_{T,p}$) and the volume of the system $V = (\frac{\partial Z}{\partial p})_{T,N}$ ($V_0 = (\frac{\partial Z_0}{\partial p})_{T,N}$) can be found from (40). We obtain

$$\mu = \mu_0 - \frac{1}{2}\left(\frac{\partial D}{\partial N}\right)_p (T_C - T)^2[\ln(T_C - T)]^a$$
$$- D(T_C - T)\{[\ln(T_C - T)]^a + \frac{a}{2}[\ln(T_C - T)]^{a-1}\}\left(\frac{\partial T_C}{\partial N}\right)_p \quad (44)$$

and

$$V = V_0 - \frac{1}{2}\left(\frac{\partial D}{\partial p}\right)_N (T_C - T)^2[\ln(T_C - T)]^a$$
$$- D(T_C - T)\{[\ln(T_C - T)]^a + \frac{a}{2}[\ln(T_C - T)]^{a-1}\}\left(\frac{\partial T_C}{\partial p}\right)_N \quad (45)$$

where we have taken into account that $T_C = T_C(p, N)$. It is easy to see that according to (44) and (45) we find

$$\Delta\left(\frac{\partial\mu}{\partial T}\right)_{p,N} = \left(\frac{\partial D}{\partial N}\right)_p (T_C - T)\{[\ln(T_C - T)]^a + \frac{a}{2}[\ln(T_C - T)]^{a-1}\}$$
$$+ \left(\frac{\partial T_C}{\partial N}\right)_p D\{[\ln(T_C - T)]^a$$
$$+ \frac{3a}{2}[\ln(T_C - T)]^{a-1} + \frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\}, \quad (46)$$

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$$\Delta\left(\frac{\partial V}{\partial T}\right)_{p,N} = \left(\frac{\partial D}{\partial p}\right)_{N}(T_C - T)\{[\ln(T_C - T)]^a + \frac{a}{2}[\ln(T_C - T)]^{a-1}\}$$

$$+ \left(\frac{\partial T_C}{\partial p}\right)_{N}D\{[\ln(T_C - T)]^a$$

$$+ \frac{3a}{2}[\ln(T_C - T)]^{a-1} + \frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\}, \quad (47)$$

$$\Delta\left(\frac{\partial \mu}{\partial p}\right)_{T,N} = -\frac{1}{2}\left(\frac{\partial^2 D}{\partial p \partial N}\right)(T_C - T)^2[\ln(T_C - T)]^a$$

$$-2\left(\frac{\partial D}{\partial N}\right)_{p}\left(\frac{\partial T_C}{\partial p}\right)_{N}(T_C - T)\{[\ln(T_C - T)]^a$$

$$+\frac{a}{2}[\ln(T_C - T)]^{a-1}\}$$

$$-D\left(\frac{\partial T_C}{\partial p}\right)_{N}\left(\frac{\partial T_C}{\partial N}\right)_{p}\{[\ln(T_C - T)]^a$$

$$+\frac{3a}{2}[\ln(T_C - T)]^{a-1} + \frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\}, \quad (48)$$

$$\Delta\left(\frac{\partial \mu}{\partial N}\right)_{T,p} = -\frac{1}{2}\left(\frac{\partial^2 D}{\partial N^2}\right)_{p}(T_C - T)^2[\ln(T_C - T)]^a$$

$$-2\left(\frac{\partial D}{\partial N}\right)_{p}\left(\frac{\partial T_C}{\partial N}\right)_{p}(T_C - T)\{[\ln(T_C - T)]^a$$

$$+\frac{a}{2}[\ln(T_C - T)]^{a-1}\}$$

$$-D[\left(\frac{\partial T_C}{\partial N}\right)_{p}]^2\{[\ln(T_C - T)]^a + \frac{3a}{2}[\ln(T_C - T)]^{a-1}$$

$$+\frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\} \quad (49)$$

and

$$
\begin{aligned}
\Delta \left(\frac{\partial V}{\partial p} \right)_{T,N} \;=\; & -\frac{1}{2} \left(\frac{\partial^2 D}{\partial p^2} \right)_N (T_C - T)^2 [\ln(T_C - T)]^a \\
& -2 \left(\frac{\partial D}{\partial p} \right)_N \left(\frac{\partial T_C}{\partial p} \right)_N (T_C - T)\{[\ln(T_C - T)]^a \\
& +\frac{a}{2}[\ln(T_C - T)]^{a-1}\} \\
& -D[\left(\frac{\partial T_C}{\partial p} \right)_N]^2 \{[\ln(T_C - T)]^a + \frac{3a}{2}[\ln(T_C - T)]^{a-1} \\
& +\frac{a(a-1)}{2}[\ln(T_C - T)]^{a-2}\}
\end{aligned}
\tag{50}
$$

where, as before, $\Delta X \equiv X(T) - X_0(T)$. It is easy to see that dividing (46)-(50) by (39) with the use of (43) and taking the limit $T \rightarrow T_C^-$ we obtain exactly the same critical relations (18)-(22) and also (24)-(26). The calculations in the case $T > T_C$ are quite similar to the case $T < T_C$ and we do not repeat them here. They also lead to the same results (18)-(22) and (24)-(26) where the limit $T \rightarrow T_C^-$ should be replaced by $T \rightarrow T_C^+$. In the other words, similarly to the preceding Section, we can simply use the limit $\lim_{T \rightarrow T_C}$ in these expressions. The case of the system at constant volume V can be treated parallel to the lines desribed above and in the preceding Section. It, however, leads again to exactly the same critical relations (30)-(37). Thus, we see that in the case of the specific heat anomaly (2) and (38) the same critical relations are valid.

4   Conclusions

Using the phenomenological approach to second order phase transitions we have shown that independent from the type of the considered system the critical relations (cross-relations) derived in this paper are exactly the same for all of them. We have shown in this way that quite different systems possess the same universal critical behaviour of the quotients. It, however, means that the exact critical relations, derived in this paper, define a new class of universal, critical relations valid for a very large number of magnetic, ferroelectric or supercon-ducting systems including also uniaxial ferroelectrics and liquid He^4.

5   Appendix A

Because of the thermodynamic relation

$$
\Delta c_{p,N} = T \left(\frac{\partial \Delta Z}{\partial T} \right)_{p,N}
\tag{A. 1}
$$

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we can write

$$\Delta S = \int \frac{\Delta c_{p,N}}{T} dT + C_1(p, N) \qquad (\text{A. 2})$$

where $C_1(p, N)$ is an arbitrary constant. In the vinicity of the critical point the condition $\frac{(T_C - T)}{T_C} \ll 1$ is fulfilled and therefore we can write

$$\frac{1}{T} = \frac{1}{T_C - (T_C - T)} = \frac{1}{T_C} \cdot \frac{1}{1 - \frac{(T_C - T)}{T_C}} = \frac{1}{T_C} \sum_{l=0}^{\infty} \frac{(T_C - T)^l}{T_C^l}. \qquad (\text{A. 3})$$

Thus, we obtain (see the formula (3))

$$\Delta S = \frac{A(p,N)}{T_C} \sum_{l=0}^{\infty} \frac{1}{T_C^l} \int (T_C - T)^{l-\alpha} dT + C_1(p, N)$$

$$= -\frac{A(p,N)}{T_C} \sum_{l=0}^{\infty} \frac{(T_C - T)^{l-\alpha+1}}{T_C^l(l-\alpha+1)} + C_1(p, N) \qquad (\text{A. 4})$$

Because $\alpha < 1$ the first term in (A.4) is going to zero at $T = T_C$. At the critical point $\Delta S = 0$ ($S = S_0$) and therefore the arbitrary constant $C_1(p, N)$ has to be equal to zero.

Starting from the expression (A.4) we obtain

$$\Delta Z = -\int \Delta S dT + C_2(p, N)$$

$$= -\frac{A(p,N)}{T_C} \sum_{l=0}^{\infty} \frac{(T_C - T)^{l-\alpha+2}}{T_C^l(l-\alpha+2)(l-\alpha+1)} + C_2(p, N). \qquad (\text{A. 5})$$

At the critical point, however, the first term in (A.5) vanishes. Because at the critical point $\Delta Z = 0$ ($Z = Z_0$) the arbitrary constant $C_2(p, N)$ has to be equal to zero. Thus, we can write the exact expression for ΔZ in the form

$$\Delta Z = -\frac{A(p,N)}{T_C} \frac{(T_C - T)^{2-\alpha}}{(2-\alpha)(1-\alpha)}$$

$$-A(p, N) \sum_{l=1}^{\infty} \frac{(T_C - T)^{l-\alpha+2}}{T_C^{l+1}(l-\alpha+2)(l-\alpha+1)} \qquad (\text{A. 6})$$

and we see that the first term (leading term) in (A.6) has the form (7) (see also (9)). This term properly reproduces the critical behaviour of the specific heat (see formula (8)) and therefore we have neglected in further considerations (see (11)-(17)) the second term in (A.6). It is, of course, possible to take into account the full expression (A.6) for ΔZ but it is completely irrelevant. The presence of the second term in (A.6) modifies the relations (11)-(17) producing very long expresions. It has, however, absolutely no influence on the critical relations (18)-(22) because the additional terms in (11)-(17) make no contributions in the limit $T \to T_C^-$ when forming the quotients (18)-(22).

6 Appendix B

Starting from the expression (39) and using (A.3) we find

$$\Delta S \quad = \int \frac{\Delta c_{p,N}}{T} dT + C_1(p,N)$$

$$= -\frac{A(p,N)}{T_C} \left[\ln(T_C - T)\right]^a \sum_{l=0}^{\infty} \frac{(T_C-T)^{l+1}}{T_C^l(l+1)} W_l(T_C - T) + C_1(p,N) \tag{B. 1}$$

where

$$W_l(T_C - T) = \sum_{m=0}^{\infty} a_{l,m} \left[\ln(T_C - T)\right]^{-m}, \tag{B. 2}$$

$$a_{l,0} = 1, \quad a_{l,1} = -\frac{a}{l+1}, \quad \dots, \quad a_{l,m} = (-1)^m \frac{a(a-1)\cdot\dots\cdot(a-m+1)}{(l+1)^m} \tag{B. 3}$$

and $C_1(p,N)$ is an arbitrary constant. The first term in (B.1) vanishes when $T \to T_C^-$ ($a = \frac{1}{3}, 1$). Because ΔS should vanish at $T = T_C$ ($S = S_0$) the arbitrary constant $C_1(p,N)$ should also be zero. Finaly we find that the exact expression for ΔZ has the form

$$\Delta Z \quad = -\frac{A(p,N)}{T_C}(T_C - T)^2 \left[\ln(T_C - T)\right]^a \times$$

$$\times \sum_{l=0}^{\infty} \frac{(T_C-T)^l}{T_C^l(l+1)(l+2)} \sum_{m=0}^{\infty} a_{l,m} \left\{ [\ln(T_C - T)]^{-m} \sum_{n=0}^{\infty} b_{l,m,n} \left[\ln(T_C - T)\right]^{-n} \right\}$$

$$+C_2(p,N) \tag{B. 4}$$

where

$$b_{l,m,0} = 1, \quad b_{l,m,1} = -\frac{a-m}{l+2}, \quad \cdot, \quad b_{l,m,n} = (-1)^n \frac{a(a-m)(a-m-1)\cdot\dots\cdot(a-m-n+1)}{(l+2)^n} \tag{B. 5}$$

and $C_2(p,N)$ is an arbitrary constant. Because the first term in (B.4) vanishes in the limit $T \to T_C^-$ the arbitrary constant $C_2(p,N)$ should be equal to zero ($\Delta Z = 0$ ($Z = Z_0$) at $T = T_C$). The expression (B.4) can be rewritten in the short form to be

$$\Delta Z = -\frac{A(p,N)}{T_C}(T_C - T)^2 \left[\ln(T_C - T)\right]^a \left\{1 + R(T_C - T)\right\} \tag{B. 6}$$

where $R(T_C - T)$ contains the terms with $l, m, n = 1, 2, \dots$ (cf (B.3) and (B.5)). The first (leading) term in (B.6) has the form of the second term in expression

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(40) where $D(p, N)$ is related to $A(p, N)$ by the formula (43). It is, in principle, possible to perform the calculation (formulae (44)-(50)) starting from the full expression (B.6). It, however, leads to extremely long formulae and therefore we have presented the results using only the leading term. The terms, generated by $R(T_C - T)$ in (B.6) produces additionally extremely long expressions in (44)-(50) which are completely irrelevant when forming the quotients (18)-(22) and taking the limit $T \to T_C^-$ because their contribution to the expressions (18)-(22) is equal to zero in this limit. Therefore the critical relation (18)-(22) are also exact in the case of the logarithmic divergence of the specific heat (39).

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